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ENERGY LEVELS AND FILLING SEQUENCES

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*ABSTRACT: The general rule of sequential (with
increasing atomic number) filling of quantum
levels by electrons is examined. It is shown
that this rule can be determined by grouping
levels on the basis of the sum of the principal
and orbital quantum numbers.*

The contemporary quantum-mechanical model of the atom, which   /115*
describes its electron shell structure, permits a reasonable expla-
nation to be given of a very large number of experimental chemical
and physical facts. Moreover, the development of theoretical con-
cepts in this field was and is constantly based on the data of ex-
perimental physics and chemistry and, in particular, on so great a
generalization of chemical (and physical) experience as D.I. Men-
deleyev's periodic law. However, this law must be admitted to be
not completely without fault, even though (from the point of view
of the congruence between the theoretical scheme and the real peri-
odic system) it fits the complex representation of the general law
of the sequential (with increasing atomic number) filling of the
quantum levels in the electron shell of the atom by electrons.

The description of this law is based on the grouping of quantum
levels by the same criterion for which the energy levels of the hy-
drogen atom in different excitation states are grouped. Since the
energy of the hydrogen atom is determined for each state by the
value of the principal quantum number, n, and (if the relativistic
correction is neglected) is independent of the orbital quantum num-
ber, l, this degeneracy is the basis for combining levels with the
same value of the principal quantum number, n, in a single group.
If this principle of grouping is applied to a multi-electron atom,
the set of electrons, occupying levels with the same value of the
principal quantum number, n, is combined in a shell (or layer) and
the general, so-called "ideal" [1] scheme of the electron levels in
atoms (which is reproduced here in Table 1) is usually presented in
conformity with this. All deviations from this scheme, i.e., from
the sequential filling of the K, L, M, N, etc. shells, are defined
as violations of the normal order of filling.

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* Numbers in the margin indicate pagination in the original text.

For those electrons occupying deeper levels in a multi-electron atom, the energy ratios justify the grouping of levels by principal quantum number: Although in a multi-electron system, the levels are not degenerate, nevertheless, in all cases, the level with the principal quantum number equal to unity (the K shell) remains deeper than any of the levels with the value of n equal to 2, 3, etc, while the levels with the principal quantum number of 2 (the L shell) are always deeper than any of the levels with the principal quantum number of 3, 4, etc. But in the peripheral part of the electron shell of multi-electron atoms, in addition to the increased number of screening electrons, the ratio between the energy level and the orbital quantum number, l, increases so much that, in a number of cases, levels with a large n, but small l, turn out to be energetically more favorable than levels with a small value of n, but a large l.

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TABLE 1. SYSTEM OF n-GROUPS OF QUANTUM NUMBERS

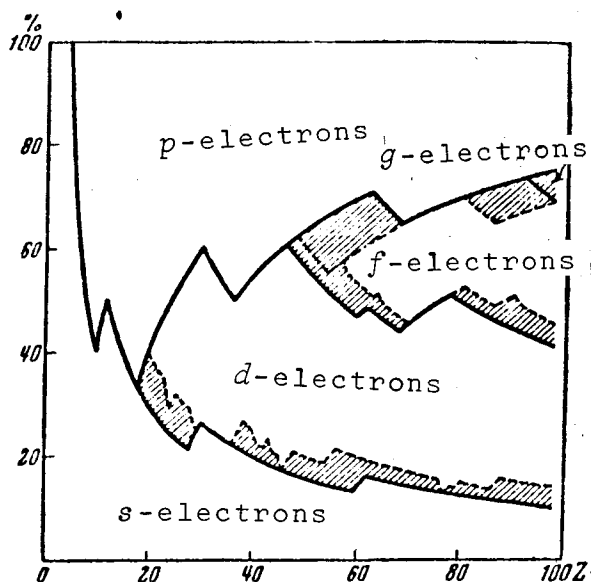| Shell Symbol (groups of levels)	Principal Quantum Number	Subgroups					Maximum Number of Electrons in Group
		$t=0$	$t=1$	$t=2$	$t=3$	$t=4$	
K	1	$1s^2$	—	—	—		2
L	2	$2s^2$	$2p^6$	—	—		8
M	3	$3s^2$	$3p^6$	$3d^{10}$	—		18
N	4	$4s^2$	$4p^6$	$4d^{10}$	$4f^{14}$		32
O	5	$5s^2$	$5p^6$	$5d^{10}$	$5f^{14}$	$5g^{18}$	50

Fig. 1. The Distribution of Electrons in Atoms. Z is the Atomic Number. The Number of s, p, d and f Electrons is Plotted on the y-Axis in Percent of the Total Number of Electrons in the Atom. The Segments of the y-Axis Between the Solid Lines Show the Distribution of Electrons that Must Occur if the K, L, M, N and O Shells are to be Sequentially Filled with Increasing Atomic Number According to the Scheme in Table 1. The Broken Lines Show the Actual Distribution of Electrons in the Atoms; the Hatching shows the Discrepancy between this Distribution and the Scheme for Sequential Filling of the K, L, M, N and O Shells.

The grouping of levels by quantum number does not reflect this specific of the energy relationships between quantum levels of peripheral electrons (in multi-electron atoms), a fact leading to considerable discrepancies between the positions of the levels in Table 1 and the sequence of their filling with electrons with increasing atomic number. For example, the $4s$ level of the N shell is filled earlier than the $3d$ level of the M shell, the $5s$ level of the O shell is filled before the $4d$ and $4f$ levels of the N shell, the $5p$ level of the O shell is filled before the $4f$ level of the N shell, the $6s$ level of the P shell is filled while the $4f$ level of the N shell and the $5d$, $5f$ and $5g$ levels of the O shell are still unfilled, etc.

The degree of discrepancy between the actual order of filling the shells and the sequence of the K, L, M, N, etc. shells is presented in Fig. 1, where the actual relationship between the number of s, p, d, and f electrons in the atoms and the relationship corresponding to the sequential filling of the n-groups of levels, according to the scheme in Table 1 are shown. This comparison shows that the distribution of electrons in the atoms is characterized not by individual "abnormal" deviations from the normal (from the point of view of the classical scheme) sequence of filling the n-groups of levels, but by a systematic regular deviation from it. This systematic deviation is attested to by a comparison between the maximum number of electrons in the n-groups of levels and the number of electrons in the periodic system, as shown in Fig. 2. The aforementioned provides the basis for formulating the following problems: What is really the general law underlying the sequential filling of quantum levels in multi-electron atoms?; could any other means of grouping formulate a reasonable system of levels which would more accurately reflect the actual sequence of their filling with increasing atomic number?
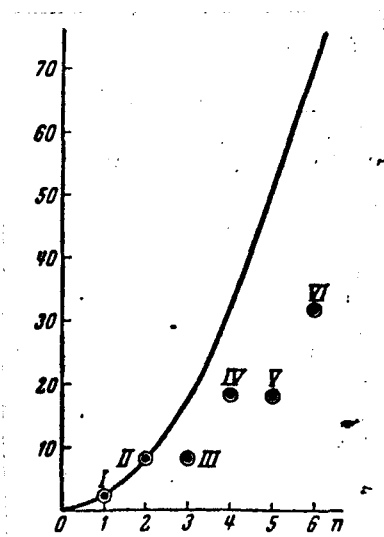

Fig. 2: The Maximum Number of Electrons in Groups of Levels with a Certain Value of the Principal Quantum Number, n, and the Number of Elements in the Periodic Table. The Curve Shows the Number of Electrons in the n-Groups of Levels, Equal to $2n^2$; the Circles show the Number of Elements in the Periods, Beginning with the Filling of Levels with the Corresponding Value of the Principal Quantum Number, the Values of Which are Plotted on the x-Axis.

A new grouping of quantum levels that would serve this purpose could actually exist, if it satisfied the following conditions: (a) in the region from hydrogen to argon, there is the same sequence of filling the levels as in Table 1, and (b) in the region from potassium to the transuranium elements, the sequence of filling the levels resulting from the new grouping should be characterized by a closer approximation to reality.

In order to examine the possibility of solving this problem, it is necessary to study the actual sequence in the filling of the electron levels in atoms with increasing atomic number. This examination shows, first of all, the existence of the following behavior, which is strictly observed throughout the periodic system: the $n_{x-1}p^6$ levels are filled before the n and s^2 levels, the $n_{x-1}d^{10}$ levels are filled before the n_x and p^6 levels, and the $n_{x-1}f^{14}$ levels are filled before the n_x and d^{10} levels, provided that the p, d, and f configurations exist at all for the corresponding values of the principal quantum number. It can easily be seen that the behavior /118 expressed by this rule actually occurs in the periodic system. Thus, for example,

(1) The $2p$ levels of the boron-neon series are filled before the $3s$ level of sodium and magnesium;

(2) The $3p$ levels of the aluminum-argon series are filled before the $4s$ level of potassium and calcium;

(3) The $4p$ levels of the gallium-krypton series are filled before the $5s$ level of rubidium and strontium;

(4) The $3d$ levels in the scandium-zinc series are filled before the $4p$ levels of the gallium-krypton series;

(5) The $5p$ levels of the indium-xenon series are filled before the $6s$ level of cesium and barium;

(6) The $4d$ levels of the yttrium-cadmium series are filled before the $5p$ levels of the indium-xenon series;

(7) The $6p$ levels of the thallium-radon series are filled before the $7s$ level of francium and radium;

(8) The $5d$ levels of the lutetium-mercury series are filled before the $6p$ levels of the thallium-radon series;

(9) The $4f$ levels of the cerium-ytterbium series are filled before the $5d$ levels of the lutetium-mercury series.

Since the subgroups of the s, p, d, and f levels correspond to values of the orbital quantum number equal to 0, 1, 2, and 3, respectively, the rule given above can be generalized in the following manner: the filling of the ns^2 level completes the sequential fil-

ling of the group of levels characterized by the same value for the sum of the principal and orbital quantum numbers, i.e., $n + l$.

Thus, an examination of the actual sequence in the filling of electron levels with increasing atomic number leads to a new concept of groups of levels, linked by the value of the sum of the principal and orbital quantum numbers, $n + l$. In order to construct a general scheme for the sequential filling of electron levels with increasing atomic number with this principle of grouping, it is necessary, in addition to the aforementioned behavior, which determines the order of the filling the s, p, d, and f levels for a group with a certain value of $n + l$, to establish the order of transition from the filling of the levels of one such $(n + l)$-group to the next. This occurs as follows: after the filling of the group of levels with the smaller value of the sum of $n + l$, the $(n + l)$-group of levels with a sum of $n + l$ (that is, one unit higher), is filled. This sequence is also observed throughout the periodic table. Thus:

(1) The $2s$ level of lithium and beryllium (sum of $n + l = 2$) is filled after the $1s$ level of the hydrogen-helium series (sum of $n + l = 1$).

(2) The $2p$ levels of the boron-neon series (sum of $n + l = 3$) are filled after the $2s$ level of lithium and beryllium (sum of $n + l = 2$).

(3) The $3p$ levels of the aluminum-argon series (sum of $n + l = 4$) are filled after the $3s$ level of sodium and magnesium (sum of $n + l = 3$).

(4) The $3d$ and $4p$ levels of the series from scandium to krypton (sum of $n + l = 5$) are filled after the $4s$ level of potassium and calcium (sum of $n + l = 4$).

(5) The $4d$ and $5p$ levels of the yttrium-xenon series (sum of $n + l = 6$) are filled after the $5s$ level of rubidium and strontium (sum of $n + l = 5$).

(6) The $4f$, $5d$, and $6p$ levels of the series from lanthanum to radon (sum of $n + l = 7$) are filled after the $6s$ level of cesium and barium (sum of $n + l = 6$).   /119

(7) The $5f$ and $6d$ levels of the actinide series (sum of $n + l = 8$) are filled after the $7s$ level of francium and radium (sum of $n + l = 7$).

Thus, it develops that the actual sequence of the filling of quantum levels by electrons is governed by a specific rule that can be defined as follows [2]:

(1) The filling of quantum levels by electrons with increasing atomic number occurs sequentially from groups of levels with a

smaller value of the sum of the principal and orbital quantum numbers ($n + l$) and groups of levels with a larger value of this sum.

(2) Within each ($n + l$)-group, the levels are filled sequentially from subgroups with a smaller value of the principal quantum number, n, and a larger value of l to subgroups of levels with a larger value of n and a smaller l.
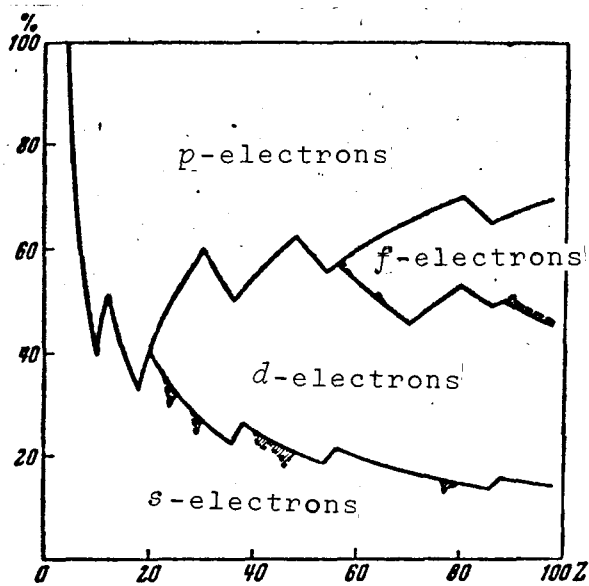

Fig. 3: The Distribution of Electrons in Atoms. The Atomic Number is Plotted along the x-Axis and the number of s, p, d, and f Electrons is Plotted Along the y-Axis as a Percent of the Total Number of Electrons in the Atom. The Segments of the y-Axis between the Curves Correspond to the Distribution of Electrons Responsible for the Sequence of the Filling of ($n + l$)-groups of Levels on the Basis of the Scheme in Table 2. The Actual Distribution of the Electrons Completely Coincides with this Sequence, Except for the Cases Indicated by Hatching.

The overall order of the sequence of the filling of quantum levels that corresponds to the rule formulated in the present paper can be conveniently represented by the system of ($n + l$)-groups shown in Table 2. The distribution of the s, p, d, and f electrons in the atoms, responsible for this sequence, and its agreement with experimental data are shown in Figure 3. A comparison of Fig. 1 and 3 shows how much more accurately (in comparison to the generally-accepted scheme) the sequence of filling of ($n + l$)-groups of levels reflects the real regularity, inherent in the periodic system, resulting in the proportion between the s, p, d, and f electrons in the atoms as a function of the atomic number of the element.

Table 2 shows that one special feature of the ($n + l$)-groups of levels is their pairing. The reason for this is that the maximum value of l in each ($n + l$)-group cannot be greater than $n-1$, while, at the same time, it can only have integral values. In view of this, the maximum number of electrons in an ($n + l$)-group of levels is determined by different formulas for odd and even values of $n + l$, being $\frac{1}{2}(n + l)^2$ in groups with an even value of ($n + l$) and $\frac{1}{2}(n + l + 1)^2$ in groups with an odd value of the sum $n + l$.

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TABLE 2. THE SYSTEM OF $(n + l)$-GROUPS OF QUANTUM LEVELS

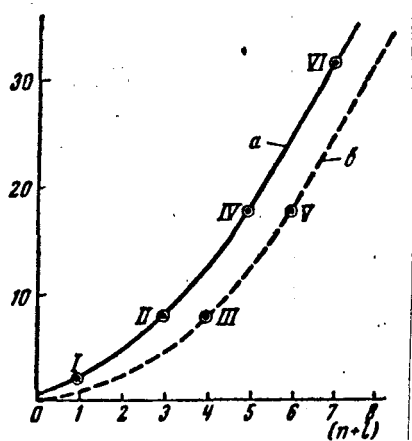| Sum of the principal and orbital quantum numbers $(n+l)$;	Subgroups				Maximum number of electrons in group.
	$l = 3$	$l = 2$	$l = 1$	$l = 0$	
1	---	---	---	$1s^2$	2
2	---	---	---	$2s^2$	2
3	---	---	$2p^6$	$3s^2$	8
4	---	---	$3p^6$	$4s^2$	8
5	---	$3d^{10}$	$4p^6$	$5s^2$	18
6	---	$4d^{10}$	$5p^6$	$6s^2$	18
7	$4f^{14}$	$5d^{10}$	$6p^6$	$7s^2$	32
8	$5f^{14}$	$6d^{10}$	$7p^6$	$8s^2$	(32)

Fig. 4: The Maximum Number of Electrons in an $(n + l)$-Group of Levels and the Number of the Elements in the Periodic System. Curve a Shows the Maximum Number of Electrons in an $(n + l)$-Group of Levels With an Odd Value of the Sum $(n + l)$, Which is Equal to $0.5 (n + l + 1)^2$; Curve b Shows the Maximum Number of Electrons in an $(n + l)$-Group of Levels With an Even Value of the Sum $(n + l)$, Equal to $\frac{1}{2}(n + l)^2$. The Circles Show the Atomic Numbers of the Elements that Complete the Filling of the Subgroup of Levels with the Corresponding Value of the Sum $(n + l)$, the Value of Which is Plotted on the x-Axis.

Fig. 4 graphically depicts the relationship between the maximum number of electrons in an $(n + l)$-group of levels and the value of $n + l$. This is expressed, on the basis of the foregoing, by two curves, one for groups with odd values of $(n + l)$ and the other for groups with even values of $(n + l)$. This same figure shows the number of elements in the periodic system, each of the periods on the x-axis corresponding to the value of $n + l$ for that subgroup of levels whose filling completes the period.

Fig. 4 shows that there is a strict relationship between the number of elements in the periodic table and the maximum number of electrons in an $(n + l)$-group of levels. This fact results in a completely determinant correlation between the boundaries of the periods and the boundaries for the filling of the $(n + l)$-groups of

levels, as was demonstrated in Table 3. It follows from this table
that, in general, levels belonging to no more than two mixed $(n + l)$
groups are filled in each period of the periodic system, while the
end of a period directly precedes the beginning of the filling of
the s level of each $(n + l)$-group, beginning with the second group.
Since the second $(n + l)$ in group $(n + l = 2)$ has no f, d, or p
levels, the first period has the property of starting and ending
with the filling of the levels of only the first $(n + l)$-group. All
the remaining periods begin with the filling of the s level of one
$(n + l)$-group and end with the filling of the p levels of the next
$(n + l)$-group (with a value of $n + l$ that is one unit higher).
Therefore, the transition to the new period with higher atomic num-
bers occurs after the completion of the first and each subsequent
odd (in atomic number) period.

TABLE 3. SEQUENCE OF THE FILLING OF THE $(n + l)$-GROUPS
OF LEVELS AND THE PERIODS IN THE PERIODIC SYSTEM

$n+l$	Levels	Periods of elements (according to their atomic number)		Periods
1	1s	H — He	(1—2)	I
2	2s	Li — Be	(3—4)	II
3	2p	B — Ne	(5—10)	
	3s	Na — Mg	(11—12)	III
4	3p	Al — Ar	(13—18)	
	4s	K — Ca	(19—20)	IV
5	3d 4p	Sc — Kr	(21—36)	
	5s	Rb — Sr	(37—38)	V
6	4d 5p	Y — Xe	(39—54)	
	6s	Cs — Ba	(55—56)	VI
7	4f 5d 6p	La — Em	(57—86)	
	7s	Fr — Ra	(87—88)	VII
8	5f 6d...	Ac — (Cf)	[89—(100)]	

Table 3 clearly illustrates this relationship between the over-
all regularity in the sequence of the filling of $(n+l)$-groups of
quantum levels and Mendeleyev's periodic law. A more detailed table
showing the configuration of each element was given in [2], where
there also appeared cases of partial deviations from the normal con-
figuration (like $s^1 d^5$ instead of $s^2 d^4$ in chromium, $s^1 d^{10}$ instead of
$s^2 d^9$ in copper, silver, and gold, d^1 instead of f^1 in lathanum and
actinium, etc.) responsible for the deviations in the distribution
of electrons which are designated by the hatching in Figure 2.

It should be noted that some of the discrepancies result be-
cause the configurations have not been established with complete
accuracy. In a number of cases, the earlier hypothesized config-
urations (as, for example, for the rare-earth elements and the ac-
tinides) were reexamined on the basis of experimental data [3] and

curiously this reexamination did not increase, but decreased the number of deviaitons from the scheme given here. One should not eliminate the possibility that their number will be further reduced in future.

However, independent of this, it can be regarded as firmly established that the sequence of the filling of quantum levels, as formulated by $(n+l)$-grouping, reflects a real general rule, inherent in the periodic system; the extent of the fractional discrepancies from the normal (from the point of view of this regularity) configurations are, as one can see from Figure 3 and by comparing it with Figure 1, many times smaller than the discrepancies between the actual order of filling the levels and the so-called "idealized" scheme, in which they were described earlier as "anomalies" of the periodic system.

CONCLUSIONS

(1) A new principle is proposed for grouping electron levels of atoms, based on combining levels with the same value of the sum of the principal (n) and orbital (l) quantum numbers in a single group.

(2) It is shown that the application of this principle of grouping permits the formulation of a rational system of atomic electron levels that reflects the actual regularity of the sequential filling of levels with increasing atomic number, not only at the beginning of the periodic table, but throughout the whole system.

(3) The filling of electron levels with increasing atomic number occurs sequentially from groups of levels with a smaller value of the sum of the principal and orbital quantum numbers $(n+l)$ to groups of levels with greater values of this sum.

(4) Within each $(n+l)$-group, the filling of the levels occurs sequentially from subgroups with a smaller value of the principal quantum number, n, and a larger value of l to subgroups of levels with a larger value of n and a smaller value of l. The filling of the levels in an $(n+l)$-group is completed by the s electrons, after which the filling of the next $(n+l)$-group begins.

(5) The maximum number of electrons occupying the levels of a single $(n+l)$-group increases with the increasing value of $n+l$, not continuously, but step-wise in the following sequence: 2, 2, 8, 8, 18, 18, 32; this includes the repetitions of 8 and 18 that are characteristic of the periodic system.

(6) In each period of the periodic system, levels belonging to no more than two mixed $(n+l)$-groups are filled, while the boundaries of the filling of the $(n+l)$-groups of levels and the boundaries of the periods (beginning with the second) are shifted only by two s electrons, since all periods which end with the filling of the p levels begin with the filling of the s level of the preceding $(n+l)$-group.

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